ASD-TDR-62-241

ELECTRODE DEVELOPMENT PROGRAM

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# NOTICES

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# FOREWORD

## ABSTRACT

This report covers the third phase of a program relating to the development of a thermally-regenerative lithium hydrogen fuel cell. Emphasis is placed on improvement of the solid columbium hydrogen diffusion electrode and methods for improving its performance. Various procedures are examined for purification of the operating media and for testing their purity. An all-columbium fuel cell is described, and the result of a successful test run embodying the data developed during the purification studies is presented.

Data are included for the various test steps, and the information is analyzed and discussed.

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# 1.0 SUMMARY

An investigation was carried out to determine methods of improving the performance of a solid columbium diffusion diaphragm when used as the hydrogen electrode in a lithium-hydrogen fuel cell. Treatments were devised for purification of the process media and preparation of the electrode, and a confirmatory run was conducted in an all-columbium fuel cell. In this run a current density of 1,400 amps per square foot was realized at 50 percent of open circuit voltage; at 68 percent of open circuit voltage--0.325 volts--at a current density of 1300 amps per square foot, a power density of 400 watts per square foot was achieved. Under short-circuit conditions, a current density of 3,500 amps per square foot was obtained.

In earlier work the concept of employing a thin diaphragm of hydrogen-permeable metal as the gas electrode has been shown to be feasible. Of the more permeable metals only iron and columbium were compatible with the fused halide electrolyte, but columbium, with a theoretical hydrogen permeability one thousand times greater than that of iron, had behaved poorly, producing only small currents at low voltages. It was postulated that columbium, with its great affinity for oxygen at elevated temperatures, was sequestering water from the hydrogen, and oxygen compounds contained in the fused salt electrolyte, to form a non-permeable oxide block on its surface.

In the present program three purification studies were carried out. To test the results of the various treatments, we exposed samples of columbium of known, low, oxygen content to the test media at a temperature of 1150°F for four hours. Subsequent oxygen analysis then could indicate the effectiveness of the treatments.

Methods of cleaning the columbium were studied and it was found that a simple soap and water wash, followed by an acetone rinse, was effective, and starting oxygen contents of the standard specimens were found to be approximately 0.020 percent.

Various procedures involving vacuum-drying, vacuum-melting, ball milling, and "gettering" with columbium turnings were investigated. It was found that the oxygen content of test samples exposed to salt which had been vacuum-dried, but with no other treatment, increased from 0.012 percent to 0.61 percent, a factor of fifty. By a combination of ball-milling, cold vacuum drying, and gettering of the salt, the oxygen content of the test samples was reduced to 0.016 percent, indicating near-perfect purification.

A purification study of process gases--argon and hydrogen--was then undertaken. At first the results were confusing and sporadic until it was found that the leak rate and ultimate vacuum obtainable in the test system were not sufficiently low, and that problems of outgassing were also present. The system was then modified with a final ultimate pressure of 0.01 micron of mercury being obtained with an apparent leak rate of 0.1 micron per hour. In a calibration run under vacuum at 1150°F, the oxygen content of a columbium test sample rose from 0.020 percent to only 0.021 percent, an indication that the system was satisfactory.

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Both hydrogen and argon were purified by passage over titanium sponge at a temperature of 1550°F. Test samples of columbium were then exposed to the gases. The oxygen content of the sample exposed to unpurified tank hydrogen was 0.41 percent, twenty times the original value. This grade of hydrogen had been used in the earlier fuel cell experiments. After exposure to gettered ultra-high purity grade hydrogen, the oxygen content was about 0.046 percent, twice the original value but still a ten-fold improvement. Exposure to purified argon raised the oxygen content from 0.020 percent to 0.024 percent, representing excellent purification. These procedures and the purification equipment were later used in the fuel cell run.

A brief study of lithium purification was undertaken. It was found that both purified and untreated lithium reduced the oxygen content of the test samples from 0.020 percent to 0.007 percent. Since lithium can be expected to deoxidize columbium at elevated temperature, these results were anticipated, and since the objective of the study was to prevent oxidation of the columbium, no problem was foreseen and the study was concluded. It is interesting to note, however, that a portion of the oxygen content of the columbium apparently exists in a layer on or near the surface, from which it can be removed by reaction with lithium.

Because of the order of operating steps it was necessary to redesign the columbium fuel cell so that the lithium anode would lie at the bottom of the electrolyte, a reverse of the earlier standard configuration. To accomplish this it was necessary to design a new anode, and the porous-columbium zero-gravity type proposed in the earlier work was investigated and tested. Good results were obtained, with the lithium uniformly wetting the porous columbium, but with no tendency to escape it by floating to the surface.

A fuel cell was built of columbium, 1.8 inches in diameter by 13-1/2 inches long. A columbium foil cathode of 0.685 inch in diameter by 0.005 inch thick was employed. It was necessary to develop and utilize special welding and brazing procedures in the assembly of the unit.

A single test cell run was performed. Because of the finite and small quantity of lithium available in the anode, the run lasted about 45 minutes. All of the purification procedures developed earlier were employed and the cathode was vacuum annealed at a temperature of 1850°F for 2 hours just prior to insertion.

Cell output was recorded on a sine wave pulse-type battery tester of conventional design, where true IR-free characteristics of the electrodes can be determined. A maximum short-circuit current density of 3,500 amps per square foot was obtained. Cell polarization was extremely low, indicated by the fact that near open-circuit voltages were recorded at current densities beyond 100 amps per square foot. The optimum power density of 400 watts per square foot was obtained at 68 percent of open circuit voltage. Of interest was the fact that in this run alone there was no initial high spurious voltage: the cell potential rose smoothly to a steady open circuit value of 0.45 volt.

Following the run, there was no apparent deterioration of the equipment. Two thin columbium structural members broke due to hydrogen embrittlement, but this was expected and can be controlled. There was no indication that the procedures of processes developed during the program could not be applied directly to an advanced fuel cell design.

## 2.0 INTRODUCTION

During two years of investigation by Thompson Ramo Wooldridge Inc., under Air Force Contract AF33(600)39573, a thermally regenerative, lithium-hydrogen fuel-cell system was developed. Operating parameters were determined, and specifications were prepared for each of the process units. Laboratory experiments have confirmed the feasibility of the system, and much valuable information was obtained regarding containment, corrosion, and handling--itself a critical aspect (References 5, 6, and 7).

Inasmuch as the system will be required to operate under a condition of zero-gravity for extended periods, it was especially important to develop electrodes which are not prone to the ills of conventional porous gas electrodes; namely bubbling of the fuel gas into the electrolyte and cessation of electrode action by capillary flooding. An entirely new approach was taken whereby the tendency of hydrogen to diffuse through selected metals at high temperature was utilized in a solid, non-porous diaphragm electrode.

Numerous studies were carried out to determine which metals offered the greatest transparency to hydrogen while remaining compatible with the exceedingly corrosive, molten-lithium metal and fluoride salts. Iron and columbium were found to be suitable in this respect; but the latter, while capable of transmitting enough hydrogen to sustain a theoretical current density in excess of 40,000 amps per square foot, gave poor performance in actual fuel cell experiments where cell output would diminish to essentially zero, usually within several minutes after startup. Consequently, iron was employed in the process development, although current densities in excess of 20 amps per square foot were seldom realized.

It had been determined that in the light of weight and volume restrictions, a current density of at least 200 amps per square foot would be required. The program which this report describes, although of short duration, was therefore undertaken to determine whether or not the true performance values of columbium could be increased to even a reasonable fraction of its theoretical capability.

Columbium, like most of the transition elements, exhibits an extraordinary affinity for the so-called interstitials--oxygen, nitrogen, carbon, and of course, hydrogen--at elevated temperatures; and the earlier work had given ample evidence that in operation the columbium electrode was simply sequestering oxygen from the process media and forming a hydrogen-opaque oxide layer on the surface. The immediate objective of this program was therefore twofold:

1. To determine means for removing the existing oxide layer from a new columbium electrode.

2. To devise methods for reducing the oxygen content of the process media below a level where contamination of the electrode could occur.

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All phases of the program were completed, and in a single test fuel cell run, the success of the treatments was spectacularly demonstrated by a current density at one-half open circuit voltage of 1,400 amps per square foot, with a brief short-circuit value of 3,500 amps per square foot. Following the run, no apparent deterioration of the cathode could be discerned.

As a useful by-product of this work, it was necessary to reduce to practice the concept introduced during the earlier program, of a porous columbium, zero-gravity, lithium electrode. The test run required that the anode be submerged in the salt rather than floating on the surface as in all previous experiments. Such an electrode was built and found to be perfectly satisfactory in every respect.

It may therefore be concluded that a solid diffusion electrode of columbium metal is capable of providing hydrogen to the cell in a usable form in quantities sufficient to sustain current densities far in excess of those presently obtainable in any other fuel cell system. It has also been shown that the zero-gravity porous columbium anode is equally effective.

## 3.0  SUPPORT FACILITIES

### 3.1  Handling

Since each of the materials used in a cell run must be treated before use, it was necessary to provide facilities whereby not only the special treatments, but also the mechanical transfer of ingredients, could be carried out in the absence of air and water.

The original "power cell" body was retained as a furnace shell, bolted to the drybox (References 5 and 7). A cylindrical heating element, thermocouple, and thermal insulation are provided inside the shell; and vacuum and argon connections enable the operation of hot test units which might otherwise collapse under vacuum or be attacked by air.

The test units--fuel cell, salt purifier, lithium purifier, and hydrogen test apparatus--are all identical in external size and shape, and by means of a flange welded around the center can be sealed to the furnace head. These units, as well as their various closures, are interchangeable, and any combinations can be provided or changed within the drybox atmosphere.

The old air-lock port was fitted with a blind flange, through which vacuum, hydrogen, argon, vent, and water-cooling leads enter the drybox. These lines were reserved only for the test units, and are independent of the vacuum-argon-vent system which serves the drybox proper. There are, therefore, three separate gas-vacuum systems, serving the furnace shell, test units, and drybox; and it is possible to provide any combination of pressure or atmosphere in any of these areas independently.

In the final work a revised vacuum system was used for the test apparatus. It is equipped with a dry ice-acetone cold trap and diffusion pump, and can maintain a pressure of 0.01 microns of mercury.

A new gas supply system was built to supply argon and hydrogen to the test equipment. Separate purification trains were built for the two gases, since each was in itself the object of gas purification studies. Both were later found to be adequate as installed.

The argon purifier consists of a two-foot length of 2-inch Type 347 stainless steel pipe filled with titanium sponge and heated to about 1470°F by means of a Hevi-Duty cylindrical heater. This system was installed to replace the one-inch purifier previously used in order to prevent the flow of large volumes of gas from lowering the temperature below a useful level. In back-filling the drybox (about ten cubic feet) the getter temperature decreases to about 1380°F after five minutes, so that the new unit remains effective at all times.

The hydrogen getter is similar. It is built of one-inch Type 347 stainless steel pipe, 12 inches long, an adequate size in view of the lower flow rates. A stainless steel thermocouple well was provided at the exit end to insure that the temperature never decreased below 1380°F, the approximate decomposition temperature of titanium hydride. Were the temperature allowed to fall below this level, the titanium would form a stable hydride and thus evacuate the cathode or other test apparatus connected with it, or worse, draw air into it through the exhaust vent.

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The drybox was also generally refurbished, with new gloves and gaskets, and a leak rate of three microns per hour was obtained throughout the overall system. A special arrangement was also provided whereby the drybox gloves could be evacuated when not in use, since experiments had shown that diffusion of air and water through the neoprene gloves was the principal source of contamination.

## 3.2 Welding

Since the test fuel cell was built entirely of columbium and columbium alloys, it was necessary that special welding techniques be used to prevent the oxidation and weakening of welded joints.

All columbium-to-columbium welds were made by helium or argon arc fusion in an inert atmosphere chamber. No filler materials or fluxes were used; nor were sand-blasting or abrasives used in cleaning, since oxygen analysis had shown that these appear to leave minute intrusions of grit in the metal surface.

Two columbium-to-stainless steel joints were required in the head of the cell. Adequate fusion-welded joints cannot be made between these metals due to the precipitation of columbium-iron intermetallics which are weak and brittle. A new procedure was therefore developed wherein these joints were sweated together with pure copper in an electron-beam welding apparatus. No special cleaning techniques of fluxes were required.

Details of the columbium fusion welds are shown in Figures 3* and 4*. In Figure 5* the copper braze can be seen where the central vent tube emerges from the top of the head. Figure 6* illustrates the cathode where the 5-mil columbium diaphragm is welded to the 7/8 inch columbium shell.

## 3.3 Analysis

In this program there was neither time nor resources for the development of techniques to determine the absolute content of impurities in the materials to be studied. For many years it has been known that fused salts invariably contain oxygen in the form of numerous oxyhalide compounds, but these are unstable in the presence of air or water, so that no analytical technique has yet been found by which the true composition of the fused salt can be determined without destruction of these materials, or conversion of them into other, meaningless, forms.

From a practical standpoint, however, absolute analyses were not required. The objective of the program was to develop treatments by the use of which the columbium cell parts would not be oxidized during operation, so that any materials which after treatment did not change the composition of the columbium were considered to be adequate for their intended use.

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*These figures appear on pages 23, 24, 26, and 28

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A master lot of duPont standard-grade 0.005-inch pure columbium was used in all fuel cell research carried out in this laboratory. The manufacturer reports the following typical analysis of the ingots from which the foil is prepared:

## TABLE 1

### TYPICAL ANALYSIS OF INGOTS

|  | Percent |
|---|---|
| Oxygen | 0.020-0.025 |
| Nitrogen | 0.002-0.004 |
| Hydrogen | Nil |
| Carbon | 0.005 |
| Tantalum | 0.1 |
| Brinell Hardness Number | 65 |

Since the foil is prepared by cold-rolling, it is reasonable to expect that the oxygen content will not be significantly greater than that of the ingot.

Samples were taken from the master sheet and analyzed for oxygen content in the as-received condition. A vacuum-fusion facility, with a Leco oxygen determinator as back-up, is maintained in this laboratory. A duplicate sample was also analyzed by an independent service company. The two results are as follows:

Columbium foil as-received.

Analyzed at TRW - 0.017 percent oxygen
Analyzed at Horizons Inc. - 0.015 percent oxygen

The agreement between these two results and with the original lot analysis by duPont is excellent and may be considered reliable.

Samples were cut from the sheet and subjected to the following four cleaning procedures. Each was followed by oxygen analysis.

## TABLE 2

### CLEANING PROCEDURES

| Treatment | Oxygen Content (percent) |
|---|---|
| 1. Washed with soap and water. Acetone rinse. | 0.012 |
| 2. Washed with soap and water, acetone rinse; abraded with No. 320 carborundum cloth; acetone rinse. | 0.028 |
| 3. Washed in soap and water, acetone rinse; sandblasted (silica grit); soap and water wash; acetone rinse. | 0.14 |
| 4. Washed in soap and water, acetone rinse; 30-second acid-etch*; water rinse, acetone rinse. | 0.017 |

Although it was not apparent until the lithium purification studies (Section 4.3) were complete, a fifth form of treatment ought to be discussed here.

Samples of washed columbium (No. 1 above) were soaked in molten lithium for four hours at 1110°F, washed, and analyzed for oxygen content. Quadruplicate analyses were made of three different samples and in all twelve cases the oxygen content was 0.007 percent, well below that of the starting material.

Since thermodynamic data indicate that lithium should deoxidize columbium at elevated temperatures, these results were anticipated; however, they do confirm that a finite oxide layer exists on new columbium which is not readily removed by conventional treatments.

It is apparent from this study that of the reasonable and available pretreatments a simple soap and water wash, followed by an acetone rinse, is the simplest and most effective method.

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*The acid etch is of a standard composition used in metallographic laboratories and is composed of the following:

| | |
|---|---|
| HF (48 percent) | – 22 parts by volume |
| $H_2SO_4$ (conc) | – 15 parts by volume |
| $HNO_3$ (conc) | – 8 parts by volume |
| Water | – 55 parts by volume |

The high oxygen contents of the sand-blasted and emery-braded samples are probably due to the inclusion of grit particles in the soft columbium.

The standard procedure adopted for the remainder of the program for evaluating the success of the various purification treatments was therefore to clean columbium test samples with soap and water and an acetone rinse and to expose them to the material under test for four hours at a temperature of 1110°F, 90 degrees higher than the cell operating temperature. If subsequent analysis indicated no increase in the oxygen content of the samples, it could be considered that the treatments would be effective in actual cell operation.

## 4.0 PURIFICATION STUDIES

### 4.1 Introduction

Four studies were carried out. Three of these relate to the three system fluids, fused eutectic salt, lithium metal, and gases--the latter including both hydrogen and argon. A fourth type of treatment, mo a correctly perhaps, procedure, is also important and relates to the problems of simply cleaning the test vessels and transferring ultra-pure material from one to another without the pick-up of impurities from the sides of the vessel or from other material-handling devices.

### 4.2 Salt Purification

It has long been known that when halide salts are melted in the presence of moisture all of the water will not, as might be supposed, boil off. Some of it reacts with the salts to form compounds of the nature LIOH, LiOCl, LiOF, as well as numerous complex oxyhalides.

Laitinen, Ferguson, and Osteryoung recognized this phenomenon in their attempts to prepare mixed chloride eutectics, and have described their efforts to purify fused salts of hydrolytic decomposition (Reference 1).

Of particular interest is their observation that from a practical standpoint the principal reaction, $LiCl + H_2O = LiOH + HCl$, is non-reversible, and that is is necessary to concentrate on preventing it during melting, rather than reversing it once it has taken place.

It had been suspected during the earlier fuel cell work that one of the causes of cathode deterioration was the fact that at elevated temperatures columbium will itself deoxidize the salts according to the following typical reaction:

$$2LiOCl + Cb \longrightarrow CbO_2 + 2LiCl \tag{1}$$

The formation of this oxide layer on the columbium cathode creates a block to the diffusion of hydrogen through it. This problem was not manifested during the work with the iron diaphragm cathodes because iron oxide is reduced by hydrogen at the cell temperature (1020°F).

The salt purification work was therefore based first on preparation of a fused melt which was as nearly free of oxygen as possible, and then "gettering" it by soaking in the presence of pure columbium turnings at a temperature in excess of the cell temperature. Actually several other metals, notably zirconium, are superior getters, but they are dissolved by the eutectic salt and are thus useless in this process. Of the metals tested only columbium appears to be an effective getter without itself dissolving.

Laitenen found that if the salts were vacuum dried cold, then ball-milled to a fine powder, cold-dried again and then slowly melted under vacuum, a large part of the water was removed

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before hydrolysis could occur. He completed his processing by treatment with anhydrous HCl gas; but in view of the difficult problems in containing fused fluorides, it was hoped that this step could be eliminated by the columbium gettering. This hope was subsequently realized.

A quantity of the standard 79-21 weight proportion eutectic of lithium chloride and lithium fluoride was prepared and divided into two portions. Part A was vacuum-dried at room temperature for 72 hours at about 20 microns pressure, with a dry ice-acetone cold trap. The salt was then stored under vacuum. Part B was similarly cold-dried for five hours in a porcelain ball mill which had been leached with 1:1 hydrochloric acid, washed, and dried. The ground salt was then cold-dried for 72 hours under vacuum. Following this period there was only a negligible apparent leak rate, indicating that essentially all of the non-combined water had been removed.

The two samples, still sealed under vacuum, were transferred to the drybox along with all equipment used in the remainder of the test, and all ensuing work was performed in its atmosphere of purified argon. The drybox had previously been outgassed for 64 hours with an ultimate leak rate of 0.3 micron per minute.

The two salt samples were loaded into Armco iron crucibles which had been carefully cleaned, but which must have been coated with a thin film of rust simply from having been exposed to air. Actually this situation was desirable, since it duplicated the conditions which had existed during the earlier fuel cell runs. Thus, any contamination introduced by the crucibles would approximate the contamination which could be expected in any actual iron fuel cell, and would be added to the impurities already present in the salt and determined along with them.

The crucibles were placed in a stainless steel pot integral with the drybox, evacuated to 20 microns, and raised to a temperature of 540°F over a period of four hours under vacuum. The temperature was then increased to 1150°F over two hours to melt the salt, and the furnace was cooled. When cold, both samples were of a dark blue-grey color with a suggestion of a scum on the top. Sample B, the ball-milled salt, appeared distinctly less discolored.

Two samples of columbium foil, cleaned as described in Section 3.3 were then introduced into each crucible, and the crucibles were heated to 540°F in vacuum, and then to 1150°F under argon, where they were soaked for four hours. The samples were then removed from the molten salt and saved for oxygen analysis.

To each of the crucibles was then added a quantity of cleaned pure columbium turnings, and both were then soaked for 65 hours under argon at 1150°F, in order to examine the ability of the turnings to sequester, or "getter", the oxygen-containing contaminants from the salt. Two more cleaned columbium samples were then added to each crucible and were soaked at 1150°F for four hours. The samples were then removed from the salt, the furnace was cooled, and the drybox opened.

Both salt samples, which had been badly discolored after the original melting, were uniformly clean and white after the gettering step. Again the ball-milled salt exhibited a somewhat better appearance. The columbium turnings were grey-black in color.

After washing, the columbium test samples which had been submerged in the non-gettered salt were extremely brittle and were grey black in appearance, with a loose, powdery, black coating which could be easily rubbed off with a cloth. The test samples used in the gettered salt were perfectly ductile. Both were silvery in appearance, and except for a few small grey spots on the non-ball milled specimen, appeared unchanged from their original condition.

The oxygen contents of the eight columbium samples were determined by vacuum fusion analysis, and are as follows:

<div align="center">

TABLE 3

OXYGEN CONTENTS OF COLUMBIUM SAMPLES

</div>

| | |
|---|---|
| Cold vacuum dried; not ball milled | 0.61 percent oxygen |
| Cold vacuum dried; ball milled | 0.56 percent oxygen |
| Cold vacuum dried; not ball milled; gettered | 0.049 percent oxygen |
| Cold vacuum dried; ball milled; gettered | 0.016 percent oxygen |
| Original columbium test samples | 0.012 percent oxygen |

The value of both the ball milling and gettering steps is graphically apparent in these results. With the non-ball milled salt there is a 12.5-fold improvement after the gettering step. Corroboration of these results is provided by the corrosion experiments carried out in the previous phase of the program, where a sample of columbium soaked in hot-vacuum-dried salt in an iron crucible had gained 0.38 percent in weight. This value corresponds reasonably well with the present value of 0.61 percent. Columbium heated in iron in the presence of lithium metal indicated no gain or loss, so that apparently the lithium was providing protection in a manner similar to that of the columbium turnings.

The following conclusions are apparent from these experiments:

1. Ball milling of the raw salt apparently aids the removal of water in the subsequent evacuation. No doubt this is due to fact that the particle size is reduced, enabling water entrained in the salt crystals to diffuse more readily to the surface.

2.  The actual value of cold evacuation of the salt, as compared to other
    possible pre-treatments, is not clearly established. It is reasonable
    to expect that hydrolysis on melting will be reduced following such a
    step, but it is evident from the recent work that the non-gettered salt
    was still grossly contaminated after melting.

    It may be seen, however, that while the improvement in oxygen content
    of the columbium in the two non-gettered samples is about 25 percent
    in favor of the ball milled material, there is an improvement of 68
    percent after the gettering step. It is possible that the value of 0.51
    percent oxygen on the columbium represents a maximum value due to
    the formation of a surface coating of oxide, and that actually the
    non-milled, non-gettered salt contains even more impurity than is
    apparent.

3.  The value of "gettering" the fused salt with columbium is most obvious.
    Within experimental error of the vacuum-fusion apparatus, the oxygen
    content of the columbium sample was virtually unchanged after immersion
    in the treated salt. The value of ball milling is more apparent here.

    The fact that gettering of the ball milled salt resulted in a substantial
    improvement over the unmilled salt is curious, since there is a demon-
    strated ability of the columbium to sequester virtually all of the oxygen;
    and it might be expected that regardless of pretreatment the gettering
    step ought to be completely effective. Again, it is probable that once
    a finite layer of oxide is built up on the getter, it loses its effectiveness,
    and that in this case the getter in the unmilled salt was "consumed"
    before it could remove the last traces of oxygen.

    It is believed that this experiment represents a significant improvement
    in the state of the art of salt purification, since in no known previous
    work has such a low apparent oxygen content been achieved so readily.
    It has already been demonstrated that the tendency of columbium to
    dissolve in the mixed halide melt is essentially nil; and this feature,
    especially in view of the fact that all others of the common gettering
    agents are rapidly dissolved, makes the process even more attractive for
    a variety of applications.

4.  It is interesting to note the close correlation between visual appearance
    of the salts and columbium and the actual content of impurity. In every
    case materials that "looked good" were good. Even small changes in
    oxygen content, as between the two gettered samples, were apparent.

On the basis of this series of experiments, the salt purification studies were concluded.

## 4.3 Gas Purification

During the earlier phases of the fuel cell program commercial untreated hydrogen was employed as a fuel. This grade of hydrogen contains varying small quantities of water vapor, which was not deleterious to the iron cathodes since hydrogen at a temperature of 1020°F will both deoxidize iron and prevent the formation of iron oxide. Columbium, however, will combine with water at this temperature, according to the reaction:

$$Cb + 2H_2O \longrightarrow CbO_2 + 2H_2 \tag{2}$$

The resulting layer of oxide is extremely stable and cannot be reduced by hydrogen. Consequently, the existence of water or air in the hydrogen fuel, however minute in quantity, will eventually cause the formation of a non-permeable oxide coating on the columbium cathode. The same situation exists with argon as a cover blanket.

A study program was therefore undertaken to determine the relative purities of the gases used in the fuel cell process and to develop methods to increase their purity. The test runs were performed in the stainless steel tube furnace attached to the drybox.

The test furnace is made of 1-1/2-inch Type 347 stainless steel pipe and is provided with a one-inch stainless steel bell attached to the inlet pipe as shown in Figure 1. Prior to a test run all tools and samples are loaded into the drybox and the whole system is evacuated. To prevent the liberation of water by reaction of hydrogen with oxides on the stainless steel during the test, the tube is first annealed in a stream of dry hydrogen at a temperature of 1850°F for one hour. It is then cooled and opened to the drybox atmosphere.

The test samples consist of coupons of cleaned columbium foil, 0.005 inch by 1/2-inch by one inch. Two pieces are used per run and are suspended inside the bell from a nichrome wire. The tube is then sealed, outgassed, and heated to the test temperature of 1120°F under argon. The flow of test gas is then initiated and continued over a four-hour period, after which the tube is then evacuated for an additional hour in order ro remove hydrogen dissolved in the columbium samples. The unit is then cooled under argon and opened, and the oxygen content of the columbium samples is determined by vacuum-fusion analysis.

In the first group of tests, six runs were performed under identical conditions of temperature and time.

### TABLE 4

### GAS PURIFICATION TEST RUNS

| Run Number | Treatments | Oxygen Content of Columbium Test Samples |
|---|---|---|
| 334-95-2 | None-Pre-test analysis | 0.012 percent |
| 334-103-3 | Ultra-high purity hydrogen,* gettered over titanium at 1550°F | 0.21 (two samples) |

Drybox

Head

Removable Test
Pot. Interchangeable
With Fuel Cell

Furnace Head

Bell Containing Columbium
Test Sample for Gas Study

Furnace Shell

Heating Element

Insulating Brick

Thermocouple

Vent

Main
Vacuum
Argon
System

Vacuum Argon

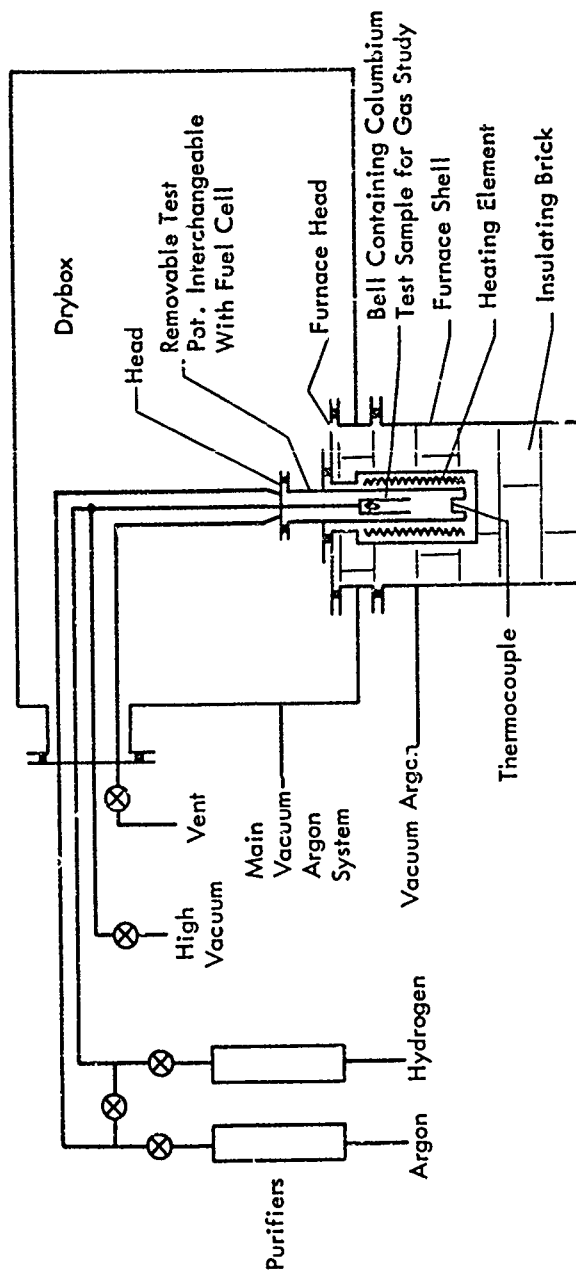High
Vacuum

Hydrogen

Argon

Purifiers

FIGURE 1  —  SCHEMATIC DIAGRAM OF GAS TEST APPARATUS

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| 334-104-2 | UHP hydrogen; not gettered | 0.47 percent |
| | | 0.48 (two samples) |
| 334-105-1 | Standard grade hydrogen; not gettered | 0.214 |
| 334-106-3A | Repeat of 103-3 above | 0.21 |
| | | 0.20 (two samples) |
| 334-109-5 | Argon, gettered over titanium at 1550°F | 0.19 |
| | | 0.22 |
| | | 0.20 |
| | | 0.22 (four samples) |
| 334-111-7 | Vacuum of 10 microns | 0.20 |
| | | 0.20 (two samples) |
| 334-110-GA | Recheck on cleaned new columbium | 0.020 |
| | | 0.020 (two samples) |

*Supplied with rated total impurity of 10 parts per million.

It can be seen that in all cases, except run 104-2, the oxygen content of the samples after exposure had increased ten-fold. It seemed extremely unlikely that gettered ultra-high purity hydrogen and ungettered standard grade hydrogen could yield the same results, as was apparently the case; and the fact that both argon and vacuum treatments also caused no change further suggested that the high oxygen contents were the result of a system or procedural failure, and could not truly reflect the relative purities of the different gases. Otherwise there was no other explanation for the very high results in run 103-2, where ungettered ultra-high purity hydrogen was used.

### 4.3.1  Conclusions

1. The two control analyses (95-2 and 110-6A) of columbium were performed at different times on samples out from different areas of the same 7-inch by 12-inch sheet from which all test pieces were taken. Considering minor variations over the sheet, and accuracy of the analysis at this low oxygen level, the analytical procedures were considered to be adequate; and it was probable that neither c these variables was responsible for the high oxygen contents in the test runs.

2. In previous fuel cell work, including these tests, the standard Kinney KS-13 mechanical pump was used as a vacuum source. The leak rate of the over-all system was about 5 microns per minute at a pressure of 15 microns. This value is not low, but calculations based on the amount of air which could possibly enter the system at this rate during the total hot period indicated that a maximum of 0.10 percent oxygen could be introduced into the columbium test sample from this cause. Thus, while a leak was probably contributory to the high results, it could not account for all of the con-tamination.

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3. In a similar program performed elsewhere in this laboratory, relating to the diffusion of hydrogen through various metals, the effect of outgassing of the system had been found to be pronounced, with extended operation at very low pressures being required before significant test results could be obtained.

It was considered probable then that outgassing problems, along with the leaks, were responsible for the uniformly high oxygen contents in the test samples.

A separate vacuum system was therefore obtained for use in the actual test portion of the apparatus. It is equipped with a dry ice-acetone cold trap and diffusion pump and is capable of maintaining the entire test region at a pressure of 0.01 micron of mercury or less. A meticulous overhaul of the entire gas-vacuum system, including getters, was then undertaken, resulting in a final total leak rate of 0.1 micron per hour.

The gas-vacuum tests were then repeated exactly as in the first test, with the following results:

TABLE 5

GAS VACUUM TEST RESULTS

| Run Number | Treatments | Oxygen Content of Columbium Test Samples |
|------------|------------|------------------------------------------|
| 334-110-GA | None – Pre-test analysis | 0.020 percent |
| -- | Furnace hydrogen annealed | -- |
| 334-114-1 | 4-hour vacuum at 1110°F | 0.021<br>0.021 (two samples) |
| -- | Hydrogen anneal of furnace | -- |
| 334-116-2 | Ultra high purity hydrogen, gettered over titanium at 1550°F | 0.042<br>0.042 (two samples) |
| 334-117-3 | Argon, gettered over titanium at 1550°F | 0.024<br>0.024 (two samples) |
| 334-118-4 | Repeat of 116-2 above | 0.047<br>0.046 (two samples) |
| -- | Hydrogen anneal of furnace | -- |
| 334-121-6 | Repeat of 116-2 | 0.064<br>0.093 |

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It appears from the consistency of the results that the difficulties in the previous series had been due to insufficient outgassing of the furnace and to the comparatively poor leak rate. The fact that a test run (334-114) carried out under vacuum for the same time and at the same temperature as all other test runs, produced substantially no change in the oxygen content of the columbium test samples indicates that no oxygen was being contributed by the system.

The oxygen content of the sample exposed to purified argon was 0.024 percent, compared to 0.020 percent before the run, indicating that near-perfect purification of the argon was achieved.

Six samples were exposed to purified ultra high purity hydrogen in three different runs. Results ranged from 0.042 to 0.093 percent. It is felt that these results are indicative of true conditions; and it is also clear that the system is extremely sensitive to the introduction of impurities during loading and outgassing. Nevertheless, although the oxygen content of the test sample doubled from 0.020 to 0.042 percent, it is still only one-tenth as high as that obtained with standard tank hydrogen (0.41 percent) of the grade used in all early fuel cell work.

## 4.4 Lithium Purification

According to thermodynamic calculation, lithium may be expected to deoxidize columbium at the cell temperature of 1020°F. If so, there would be no problem of contamination of any columbium cell parts, and the small amount of oxide in the lithium could not be expected to affect the cell performance in view of the otherwise high efficiency of the lithium metal electrode.

An experiment was therefore performed to evaluate this calculation and to study the effect of known purification procedures. The best available procedure for purification of lithium of oxygen and nitrogen is that of Hoffman (Reference 2) who recommends soaking the metal for 24 hours at 1500°F in the presence of yttrium and titanium metals. The former readily sequesters oxygen from the lithium, and the latter, nitrogen.

Both crucibles were soaked at 1500°F for 40 hours, in order for the lithium to be gettered as well as possible. Following the soaking, the metal in both crucibles was exceptionally silvery in appearance with no trace of color or scum. A sample of cleaned columbium was then placed in each crucible and soaked for four hours at 1110°F, the standard conditions used in all purification studies. A similar run was also performed with unpurified, as-received lithium.

Analysis of the three samples, each run in quadruplicate, indicated an oxygen content in every case of 0.007 percent. It was thus confirmed that the lithium, regardless of its own purity, was able to deoxidize the columbium test-samples. It was also apparent, in view of the fact that the oxygen content of the test samples was reduced to approximately one-third its original value, that a considerable portion of the oxygen in the columbium exists as a surface layer which cannot readily be removed.

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## 4.5 Equipment Cleaning

In any system, regardless of the method of pre-cleaning, there will remain on the surface of the metals a finite, though thin, layer of oxide due to contact with the air. Unless this oxygen can be caused to dissolve into the metal, as by vacuum annealing columbium, it can be fluxed from the surface by the electrolyte salts and thus introduce a contaminant in the form of oxyhalides which can re-contaminate the cathode. The mere exposure of virtually any structural metal, however clean, to air will oxidize it, and a serious problem could therefore exist in the construction of a practical fuel cell.

The approach taken in this program to resolve this problem has already been described in connection with the salt purification studies (Section 4.2). It consists of cleaning the equipment insofar as is practical by conventional methods, but with no special care being taken to prevent oxidation before actual use. The approach taken is that any contaminant which the salts cannot remove from structural metals or from any adventitious impurities introduced during assembly, will not harm the cathode. Each crucible used in the salt tests was of course soaked in fused eutectic. In the last step of purification columbium turnings were present in the crucibles, and these removed not only the oxygen compounds originally present in the salt, but also those introduced from the crucible itself. The crucible walls were then presumably perfectly free of available oxygen and could not thereafter be exposed to air without recontamination.

Even the process of pouring purified salt from one vessel to another could present a problem unless the transfer tube, or lip of the crucible, could first be treated. Since this was not practicable in the recent work, the cell was designed so that the vacuum-annealed cathode would be inserted last. A quantity of columbium turnings was placed in the bottom of the cell, itself made of columbium, so that in the final heat-up before operation any last traces of oxygen from the crucible walls, or any other source, would be removed. The procedure appeared to be completely effective.

## 5.0 CONFIRMATORY FUEL CELL OPERATION

### 5.1 Equipment

### 5.1.1 Cell Body

To test the results of the purification studies, we built an all-columbium fuel cell. An important aspect of the test run was to have all test units and their respective heads or closures fully interchangeable, and thus the dimensions of the cell were fixed at 1.9 inches O.D. by 13-1/2 inches long, the same as the stainless steel pots that were used in the purification studies.

Unalloyed columbium of high purity is difficult to obtain on short notice, and it was necessary to form the shell from a single sheet of 0.050-inch columbium of the duPont standard grade. Tubing of this diameter cannot be formed on available rolls, and a set of wood forming dies was made and calibrated by forming several practice tubes of mild steel.

The columbium sheet as received had been 90 percent cold-worked, and was stiff and springy. Before forming it was vacuum-annealed at a temperature of 2400°F for one hour.

A drawing of the cell appears in Figure 2. The shell (1)*, bottom (2), and the end of the thermocouple well (3) are made of 0.050-inch pure columbium sheet. The thermocouple well (4) is made of 3/8-inch pure columbium tubing with a wall thickness of 0.020 inch.

A top flange (5) of the same design as used previously is provided, and a center flange (6) is used to form a vacuum-tight seal onto the furnace head (7) during operation. By means of this, seal water or air accidentally admitted to the drybox can be confined around the cold upper part of the cell while the bottom, in the furnace, is surrounded by a separate atmosphere of argon. Although these two flanges were not in contact with the electrolyte, and therefore did not need to be made of columbium, they were nevertheless made of a columbium-1 zirconium alloy in order to avoid the difficulties of dissimilar-metal welding.

The entire unit was assembled by fusion welding in an inert atmosphere chamber. Photographs of the cell body appear in Figures 3 and 4, in which the unusual fusion welds are seen to advantage.

Copper water-cooling tubes were then soldered to the upper portion of the cell body. To achieve this, the columbium wall was first tinned in the inert atmosphere chamber with an argon-arc torch.

### 5.1.2 Cathode

Continuing with reference to Figure 2, the cathode consists of a shell (8) of pure columbium 7/8 inch O.D. by 0.685 inch I.D. with a 0.005-inch disc of pure columbium foil welded

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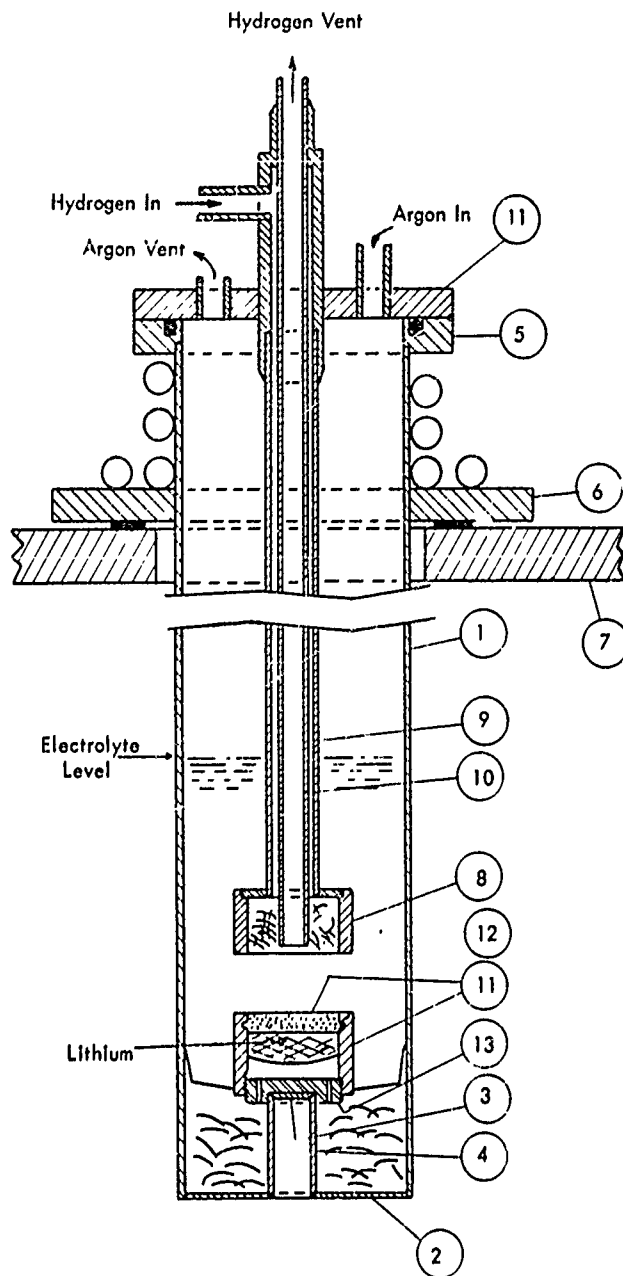
*Numbers in parenthesis refer to the numbers in Figure 2.

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FIGURE 2 — CROSS SECTION OF COLUMBIUM FUEL CELL

FIGURE 3 – COLUMBIUM FUEL CELL BODY SHOWING SEAM WELD

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FIGURE 4 - DETAIL OF COLUMBIUM FUEL BODY

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across the end. To eliminate the possibility of formation of gas pockets, as might occur with the use of a retaining ring, the columbium disc was fused directly to the cathode body. To achieve this difficult weld, a disc-shaped tungsten chill was temporarily clamped across the face, leaving only the edge exposed. The argon-arc torch was again used in the inert atmosphere chamber.

The top of the cathode was closed by a disc of pure columbium 0.050 inch thick, and the unit was mounted on a hydrogen feed tube (9) 0.375 inch O.D., 0.020-inch wall, made of columbium-10 titanium alloy. A hydrogen outlet tube (10) is also shown, made of columbium-3/4 zirconium alloy, 1/4-inch O.D. with 0.020-inch wall.

The cathode is fixed to the removable cell head (11) made of Type 321 stainless steel. The hydrogen enters through a special fitting in the top, passes through the outer tube into the cathode, and exists through the center tube. Both columbium alloy tubes were sweated into the stainless steel adaptor with pure copper, heated in the electron beam welded. By this method no brittle intermetallic compounds, of the type formed when columbium is fusion welded to iron alloys, were formed. Before final assembly the cathode shell was filled with clean columbium turnings as an added precaution against contamination by impurities in the hydrogen.

A photograph of the complete cell assembly, taken after the run, appears in Figure 5. The cathode alone, also photographed after the run, is pictured in Figure 6. The loop-shaped line on the face, as well as the generally mottled appearance of the columbium foil, are stains formed on the surface when the unit was washed after operation. Some-what surprisingly, in view of its excellent corrosion resistance, perfectly clean columbium is readily stained by salts or fingermarks. The diaphragm was clean and mirrorlike when removed from the cell, and the marks are only superficial and do not affect its integrity.

The active face of the cathode is 0.685 inch in diameter, with a total area of 0.369 square inch, or 0.00256, or 1/390th square foot.

### 5.1.3  Anode

In all of the earlier fuel cell research where the solid diaphragm was used, it was customary to place the cathode diaphragm at the bottom of the electrolyte as an integral part of the cell structure and to employ the lithium anode as a pool floating on the surface within a metal bell. Toward the end of the last phase of the program, a zero-gravity anode-separator was devised, and while it was subjected to physical tests, it was never employed as a working electrode. A three-cell breadboard regenerative system was built employing such anodes, but has not yet been operated.

In the present program it was deemed necessary to add the electrolyte salt to the cell first, allowing it to soak with columbium turnings before the cathode, which was vacuum annealed, was inserted. It was therefore necessary to reverse the former practice, by providing an anode which could be placed in the bottom of the cell before the salt was added, and which would therefore operate submerged with the active face uppermost.
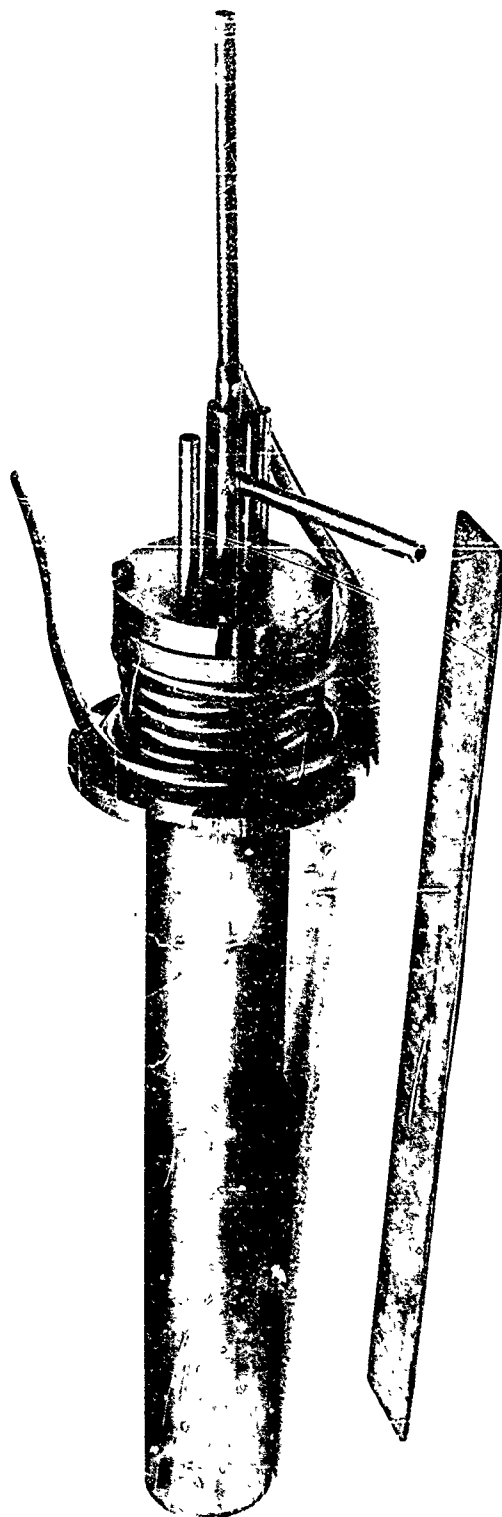
25

FIGURE 5 - COMPLETE CELL ASSEMBLY AFTER RUN

The concept developed earlier was successfully adapted to this purpose. Again with reference to Figure 2, the anode consists of a tube of pure columbium (11) 7/8-inch O.D., by 0.685 inch I.D. by 5/8 inch long, formed from the same stock as the cathode. A 1/8-inch layer of electrolytic columbium powder (12) is sintered across the active end. This was accomplished by inverting the tube on a ground tungsten plate, pouring in the loose powder as a layer, and heating to a temperature of 3400°F in vacuum. A groove machined around the inside of the tube aids in securing the porous plate, although adequate bonding seems to be possible without it.

The bottom of the anode is threaded to accommodate a plug (13) of columbium-1 zirconium alloy--bored to rest on the thermocouple well. A star of columbium foil was then tack-welded to the anode, by means of which the unit could be more securely guided into place in the cell, and, because of its spring tension against the cell wall, good electrical contact would be assured. Following the run the foil star and the porous plug were removed and a new plug was sintered into place. A photograph of the anode appears in Figure 7. The large grains visible in the photograph are due to recrystallization of the pure columbium shell during the vacuum sintering operation.

Four 3/64-inch holes are drilled in the bottom plug. In practice it was intended that the anode would be loaded with lithium metal, sealed, and placed in the cell. Because of its high surface tension, the lithium cannot leak through the holes, but when salt was added to the cell, it would enter the holes and float the lithium against the porous columbium face, which it would wet and fill, but from which it would not escape, again because of its high surface tension and tenacious wetting properties in the presence of the molten salt flux. As lithium was consumed from the surface of the anode during cell operation, capillary action would tend to replenish it by metal from the interior.

Several anode mock-ups were built and subjected to physical tests with lithium metal and fused salt. Because of the clarity of the molten salt, it was possible to observe that the porous columbium surface rapidly became uniformly wetted by lithium; and shaking or jolting of the test crucible could not dislodge any droplets.

The anode configuration as developed in these tests was subsequently adapted to the fuel cell, where it operated as planned.

## 5.1.4   Electrical Test Apparatus

There is available in this laboratory an electrode test apparatus of the type described by Kordesch and Marko (Reference 3). The device is designed to measure both voltage and current under IR-free conditions, and thus eliminates losses due to internal resistance of the cell, connectors, line loss, and other factors which while they can affect the net output of any given cell design, are not really characteristic of the electrodes themselves. This type of tester is commonly employed in fuel cell research, and the results obtained from its use may be compared to those reported for other systems.

FIGURE 6 - COLUMBIUM FOIL CATHODE (0.685 INCH) AFTER RUN



FIGURE 7 - POROUS COLUMBIUM (0.685 INCH) ANODE AFTER RUN

During a test run a six volt half-wave, 60-cycle power source is connected in series with the cell. A diode gating circuit is employed to switch the connection alternately between two measuring circuits. During the pulse phase the cell, along with the power source, is connected through a variable resistor, the control of which enables the operator to determine the current passing through the cell. Since amperage is independent of resistance in a series circuit, these are no IR losses, and the true amperage is measured. The external source serves to smooth out the pulse wave, since the actual amperage of the cell is usually low owing to the small size of the test electrodes. Without it, any small fluctuations in the cell output would cause large fluctuations in the ammeter readings.

During the "off" half of the cycle, the cell is switched to a zero-load circuit containing a capacitor and a vacuum-tube voltmeter. Because the circuit is not completed, there are no IR losses and the capacitor is charged to the true IR-free potential of the cell, which is then indicated on the voltmeter.

It has been found that by rapid alternation of the measuring circuit between the pulsed load phase and the zero-load phase the voltage, being obtained within 1/120 second after the load is removed, is essentially the same as the polarization voltage of the cell under load, inasmuch as there is not time in this brief interval for the cell to recover. Thus, by manually controlling the variable resistance, it is possible to obtain a series of voltage-current curves from which all IR properties of the system are absent, and which indicates the true performance of the cell process.

## 5.2  Cell Operation

### 5.2.1  Introduction

Owing to limited time and to the irreplaceable nature of the materials from which the cell was constructed, it was expected that only a single test run could be made. It was intended that the best of the procedures developed in the earlier part of the program would be employed, and that test results would be determined on the sine wave electrode testing apparatus.

### 5.2.2  Preparation of Run

Four hundred and fifty four grams of Lithium Corporation technical grade lithium chloride and 105 grams of Lithium Corporation technical grade lithium fluoride were mixed to form the standard 79-21 eutectic electrolyte. The mixture was dried for six hours at room temperature under a vacuum of about 20 microns of mercury and then quickly transferred to a porcelain ball mill which had previously been leached in 1:1 hydrochloric acid for 8 hours, washed, and dried. The salt was then milled for 18 hours until it was finely powdered and thoroughly mixed.

The salt mix was then transferred again to the drying apparatus and evacuated to a pressure of about 10 microns for 72 hours. During this time approximately 9 grams of water accumulated in the dry ice-acetone cold trap. The salt was then preserved under vacuum.

Prior to insertion in the drybox all columbium cell parts were washed in soap and water, and the cell was subjected to an additional acid rinse. A stainless steel treating pot was then mounted in the drybox furnace, and the cell and all materials were placed in the drybox and an atmosphere of purified argon installed. Since the lithium purification experiments had shown that the lithium, regardless of treatment, would not contaminate columbium at cell conditions, standard Foote Min. al Company grade lithium in the unpurified form was prepared as a cylindrical plug weighing 1.4 grams, and inserted dry into the anode. The anode was then placed in the cell, to rest on the thermocouple well with the columbium foil "wings" forced against the cell wall. An unweighed quantity of chopped, washed columbium turnings was then placed in the bottom of the cell, rising to about the middle of the anode.

Two Armco iron crucibles, having been previously acid-cleaned and washed, were then loaded with the vacuum-dried eutectic salt and placed in the furnace. A vacuum of 0.1 micron was achieved and the temperature was then slowly raised to 850°F over 6 hours. The vacuum was then replaced with argon and the salt was raised to a temperature of 1020°F to melt it. The furnace was quickly opened (still in the drybox atmosphere) and the crucibles were emptied into two similar crucibles which had previously been half-filled with cleaned columbium turnings. These were returned to the furnace and soaked at a temperature of 1120°F for 18 hours, when again the furnace was opened and the crucibles were quickly emptied into the fuel cell. It was necessary to repeat this procedure three times to secure enough purified salt. The final cell charge was 3-1/16 inches deep and weighed approximately 184 grams. During times when the cell was not being loaded, it was covered with a temporary stainless steel head to which a source of purified argon was connected.

With the cell sealed under an argon pressure, the drybox was opened and carefully cleaned. A second stainless steel pot was installed and the cell head and cathode assembly were attached to it. The furnace was then evacuated to a pressure of 0.005 micron and the temperature was raised to 1830°F for two hours. This vacuum-annealing step causes any oxide layer on the surface of the columbium to dissolve into the interior of the metal where it no longer constitutes a block to the diffusion of hydrogen. Once a columbium part has been vacuum annealed, it is of course necessary that it not be exposed to air or water, since the oxide layer will immediately re-form even at room temperature. The annealing pot was then cooled, filled with argon, and removed from the furnace. It was set aside and the copper water-cooling lines were carefully soldered closed to prevent contamination of the drybox atmosphere during the final step.

The columbium fuel cell was then mounted in the drybox furnace. Prior to this run, the entire furnace was hot evacuated to a temperature of 1100°F for a total of 96 hours, during which time it was cooled and reheated five times in order to allow moisture in the insulating bricks to diffuse back into the heating zone, from which it could be more easily removed. A final apparent leak rate of 3 microns per minute indicated that substantially all of the water had been removed from the furnace. After the cell was mounted, the furnace was again evacuated and filled with argon. This procedure was carried out as a precaution against oxidation of the columbium cell during operation by water accumulated in the furnace insulation.

The cathode, still under argon in the vacuum annealing tube, was placed in the drybox and all electrical and gas connections were made. The hydrogen getter had been outgassed cold to a pressure of 0.02 micron for 16 hours and was heated to a temperature of 1560°F and flushed for 6 hours before operation. The drybox was closed, carefully outgassed, and filled with purified argon. During this time the electrode test apparatus was calibrated and the electrical leads were rechecked for presence of any capacitance effects. None was noted.

The cell was heated to a temperature of 1020°F and opened. With a flow of argon passing through it, the cathode was then removed from the annealing furnace and placed in the cell. The cathode had been welded to the cell head and an anode-cathode spacing of exactly 1/2-inch was maintained. The cell head was secured by means of a neoprene gasket and three insulated Vise-grip pliers. After a few moments of heat-up, a hydrogen flow was initiated to the cathode, and immediately a voltage was developed and began slowly to rise, achieving an open circuit potential of approximately 0.45 volt in a period of five minutes. The run was marked by the complete absence of the high spurious voltage which had been characteristic of every past run. The slowness of the voltage rise was probably attributable to the gradual replacement of the argon in the cathode by hydrogen.

The complete chronological run record is recorded in Table 6.

### 5.2.3  Run Summary

Five minutes after start-up, the open-circuit voltage appeared to be fairly stable at a value of 0.45, and various loads were applied to the cell. Since the endurance of the unit could not be foreseen, the first pass of voltage-current measurements was made quickly. Between each two readings the open-circuit voltage was determined and found to return almost immediately to a value of 0.45, indicating that no permanent polarization of deterioration had occurred. It may be seen in Table 6 that during the 4:20 and 4:21 readings the polarization voltage was actually slightly higher than the starting open circuit voltage, indicating that the open circuit value was still rising very slowly, and also indicating that at current densities up to 100 amps per square foot there was virtually no polarization whatever. At the end of the first pass the cell was short-circuited briefly and a current of 9 amps was obtained on the 0.685-inch cathode. This value corresponds to a current density of about 3,500 amps per square foot. Following the short-circuiting of the cell, the open circuit voltage rose to a value of 0.40 volt in 15 seconds, and in 75 seconds had risen to slightly higher than the starting value.

A second pass of voltage current readings was then made with results following nearly the same curve as did the first series. A third pass was then started and it was noted that the voltages at given loads were substantially lower. During the first phase of this program, it had been learned that lithium metal will dissolve more readily in the electrolyte when lithium hydride is also present, and owing to the heavy loads impressed on the cell with the consequent formation of large amounts of lithium hydride, and to the comparatively small amount of lithium metal present in the anode, it was suspected that the cell was becoming exhausted.

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TABLE 6

## RUN RECORD, COLUMBIUM FUEL CELL

Cell temperature - 1020°F
Cell atmosphere - argon
Cell pressure - one atmosphere
Hydrogen pressure - one atmosphere
Cathode area - 0.369 square inch
Anode area - 0.369 square inch
Anode-cathode spacing - 0.50 inch

| Time | Actual Current Amperes | IR-Free Voltage | Percent of Open Circuit Voltage | Current Density, Amps Per Sq. Ft | Power Density, Watts Per Sq. Ft. | Remarks |
|---|---|---|---|---|---|---|
| 4:15 | 0 | 0 | - | - | - | Start of hydrogen flow |
| 4:16:20 | 0 | - | - | - | - | Thermal voltage 0.30 |
| 4:17 - | 0 | - | - | - | - | Thermal voltage 0.36 |
| 4:18 - | 0 | - | - | - | - | Thermal voltage 0.40 |
| 4:19 - | 0 | 0.43 | - | - | - | Thermal voltage 0.44 |
| 4:20 | 0.030 | 0.45 | 100 | 11.7 | 5.5 | |
| | 0.042 | 0.445 | 99 | 16.4 | 7.3 | |
| | 0.056 | 0.45 | 100 | 21.9 | 9.9 | |
| | 0.084 | 0.458 | 101 | 32.7 | 15.0 | |
| 4:21 | 0.114 | 0.458 | 101 | 45.5 | 20.8 | |
| | 0.150 | 0.455 | 100 | 52.2 | 26.4 | |
| 4:23 | 0.200 | 0.450 | 100 | 78.0 | 35.2 | |
| | 0.295 | 0.450 | 100 | 115 | 51.9 | |
| 4:24 | 0.545 | 0.440 | 98 | 213 | 94.0 | |
| | 0.820 | 0.430 | 95 | 320 | 138 | |
| 4:24:30 | 1.105 | 0.410 | 91 | 432 | 177 | |
| 4:25 | 1.95 | 0.375 | 83 | 760 | 285 | |
| 4:25:45 | 9- | - | - | 3500 | - | Load briefly short-circuited |
| 4:26 | - | 0.40 | - | - | - | No load: voltage recovering |
| 4:27 | - | 0.455 | - | - | - | No load: voltage recovering |
| 4:28:15 | 0.30 | 0.440 | 98 | 117 | 51.5 | |
| 4:29 - | 0.835 | 0.425 | 94 | 326 | 138 | |
| 4:29:28 | 1.80 | 0.385 | 86 | 700 | 270 | |
| 4:30 | 1.80 | 0.375 | 83 | 700 | 252 | During this period |
| 4:30 | 3.10 | 0.325 | 72 | 1210 | 393 | the open-circuit |
| 4:31:30 | 3.60 | 0.240 | 53 | 1400 | 336 | voltage returned |
| 4:32 | 0.30 | 0.240 | 53 | 117 | 28.2 | to 0.45 after |
| 4:32:45 | 0.82 | 0.210 | 47 | 320 | 67 | removal of loads. |
| 4:35:30 | 0.82 | 0.190 | 42 | 320 | 61 | |
| 4:36 | 0.80 | 0.190 | 42 | 313 | 59 | |
| 4:36:30 | 0.80 | 0.190 | 42 | 313 | 59 | |
| 4:37 | 0.80 | 0.186 | 40 | 313 | 57 | |
| 4:38 | 3.60 | 0.120 | 27 | 1420 | 172 | |

At this point a resistance was connected directly to the cell eliminating the electrode test apparatus, and a single reading of 0.300 amp was obtained at a voltage of 0.120. These values include all drops.

| | | | | | | |
|---|---|---|---|---|---|---|
| - | 0.300 | 0.120 (Not IR-Free) | 37.5 | 117 | 14.1 | |
| 4:52:15 | - | 0.080 (Not IR-Free) | - | - | - | Open circuit terminal |
| 4:54 | - | 0.080 (Not IR-Free) | - | - | - | voltage |
| 4:56 | - | - | - | - | - | Run terminated |

The electrode tester indicates the performance of the electrodes themselves, and factors of cell construction, such as internal resistances, conductivity of structural metals, and anode-cathode distance, do not affect the values as they would when the cell is actually serving as a primary power source. A variable resistance was therefore connected directly to the cell and a single reading of 0.120 volt at a current of 0.300 ampere was obtained. This value corresponds to a current density of 117 amp per square foot. Following this one reading, the cell output collapsed and the run was terminated.

The cathode was removed and examined while the cell was still hot. The foil diaphragm was mirror-like and appeared to be unchanged. In handling the cathode the columbium-zirconium shank tube broke near the cathode. This was, of course, due to hydrogen embrittlement, since it was not possible to evacuate the cell after the run. This result was anticipated. Still hot, the cell was removed from the furnace and emptied onto a steel plate. The salt was pure white, and was preserved.

Following the run, the anode was removed from the cell and all parts were washed. In removal of the anode the top of the thermocouple well broke off, again due to hydrogen embrittlement. The anode was empty of lithium, and along with all other columbium parts, appeared to be perfectly unchanged from its original appearance. A qualitative test of the salt indicated the presence of lithium hydride.

The graph in Figure 8 contains a plot of measured amperage on the 0.685-inch electrodes versus the IR-free voltage. The single current versus non-IR-free voltage value is also shown.

Current density versus percent of open-circuit voltage is plotted in Figure 9, and in Figure 10 is plotted the power density in watts versus percent of open circuit voltage.
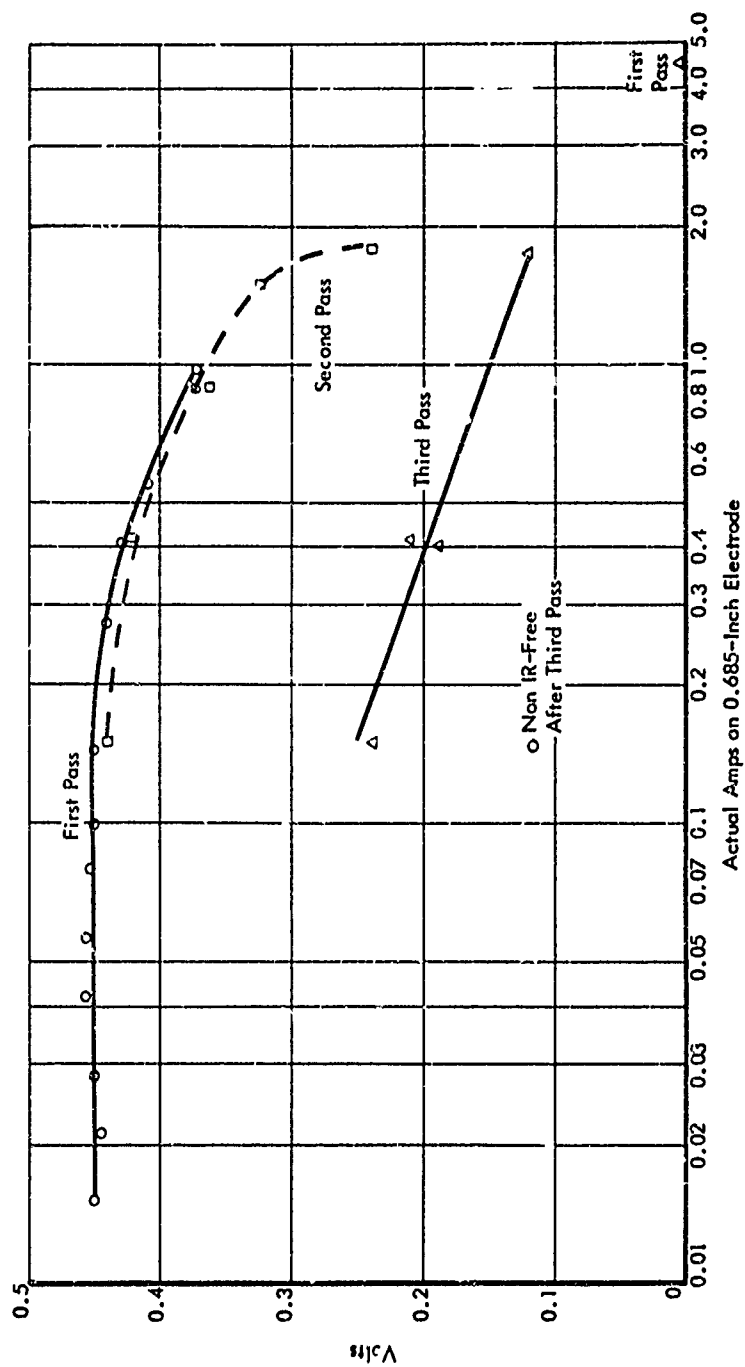
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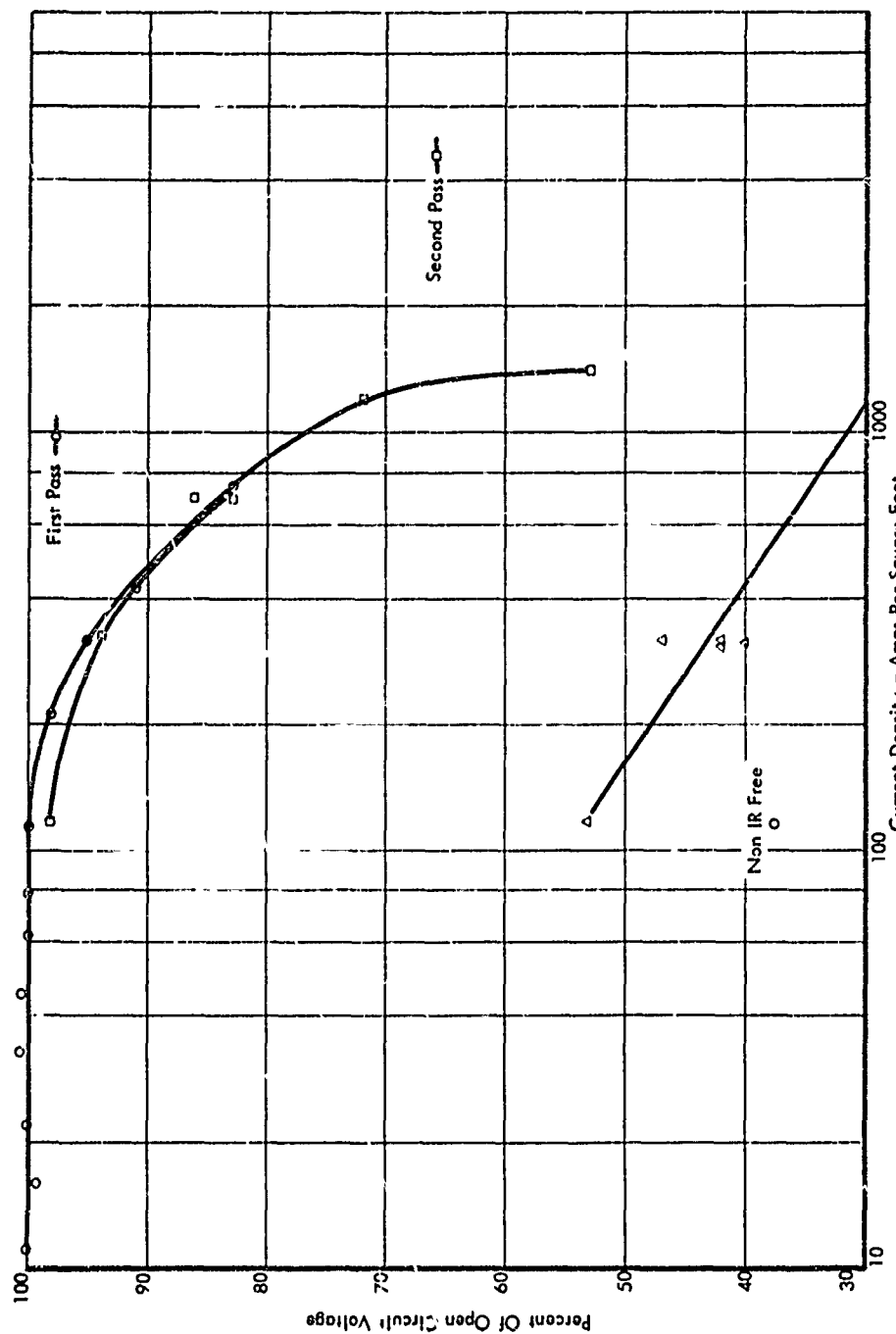FIGURE 8 — ACTUAL CURRENT VS. VOLTAGE

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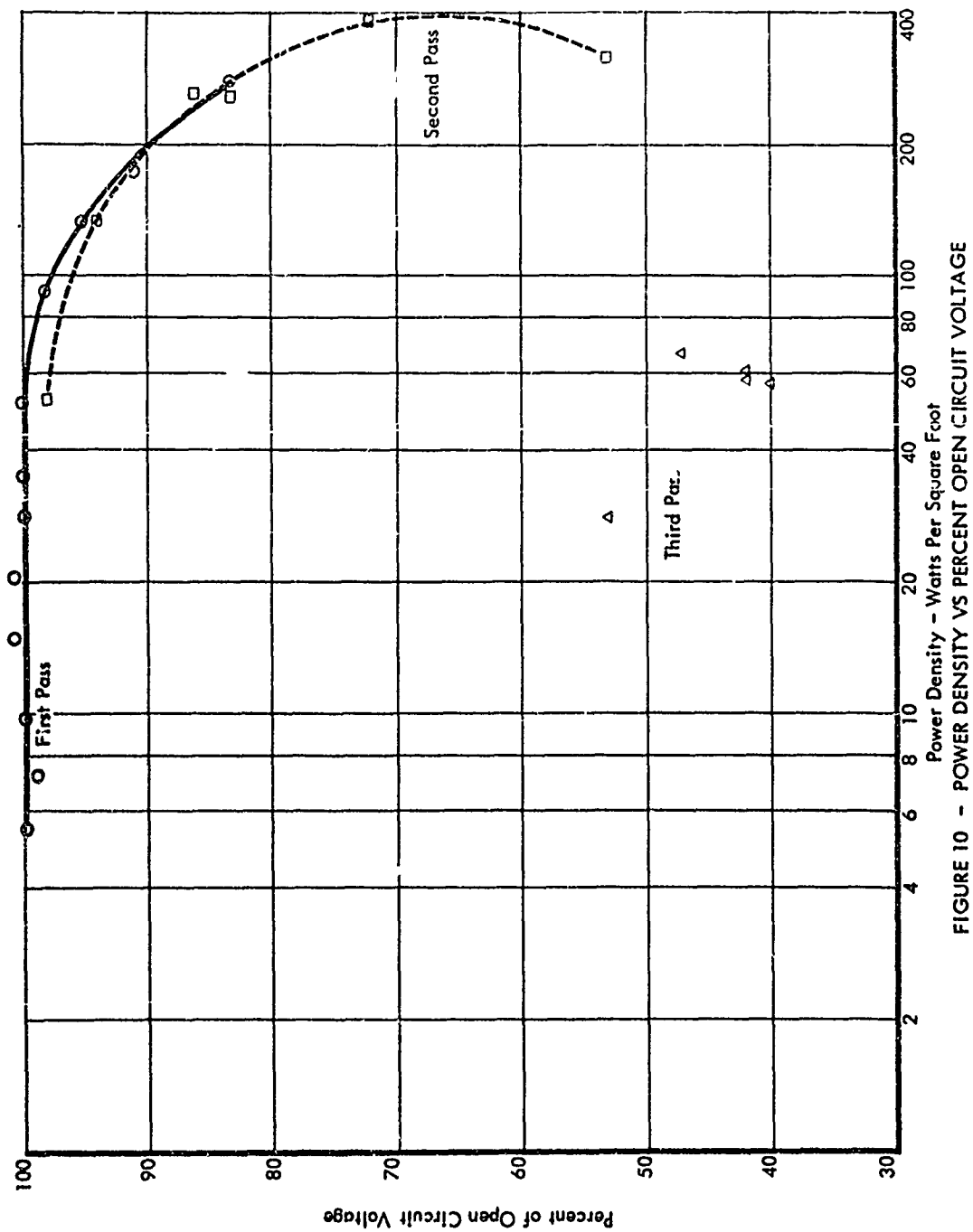FIGURE 9 – CURRENT DENSITY VS. PERCENT OPEN CIRCUIT VOLTAGE

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FIGURE 10 – POWER DENSITY VS PERCENT OPEN CIRCUIT VOLTAGE

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## 6.0 CONCLUSIONS

1. It has been demonstrated that under properly controlled conditions a solid diaphragm of columbium metal may be used as a cathode in the lithium-hydrogen fuel cell, and that useful current densities in excess of 1400 amps per square foot can be obtained.

2. As a result of the second pass of this one run, it appears that maximum power densities are obtained at about 68 percent of open circuit voltage. At this level a power density of approximately 400 watts per square foot was obtained at a current density of 1300 amps per square foot and a potential of 0.325 volt.

3. A particularly interesting conclusion which may be drawn concerns the relative activity of the foil diaphragm electrode when compared to a porous type gas electrode. The total surface area of the latter is many thousands of times that of the foil diaphragm; yet the current densities obtained in the two different systems are in the same order of magnitude, with the flat foil surface actually providing superior results. This fact may be useful in the evaluation of porous electrodes in that it suggests that the net useful area must be approximately the same as the apparent surface area, notwithstanding the enormous area within its labyrinthine structure.

4. Polarization of the columbium cathode is apparently very low. This may be seen in the fact that essentially open-circuit voltages were still obtained even at loadings up to 200 amps per square foot, and in the rapid return to open circuit conditions after loadings as high as 1400 amps per square foot were impressed. Even after a dead short circuit of the cell, at 9 amps or 3500 amps per square foot, the voltage rose to 89 percent of the open circuit value within 15 seconds after the load was removed, and to the original open circuit voltage within 75 seconds. Rapid recovery such as this is most uncommon in fuel cell electrodes, and may likely be due to the smooth electrode surface, where the tendency to polarize may be reduced owing to the absence of pockets or capillaries which tend to inhibit the migration of ions away from the active areas into the electrolyte.

5. Efficiency of the cell is also apparently high. The perfectly efficient cell would of course produce the maximum power at the maximum, or open-circuit, voltage. Generally, however, the largest power outputs are obtained at approximately 50 percent of the open circuit voltage. In the graph in Figure 10 where the power density in watts per square foot is plotted versus percent of open circuit voltage, it may be seen that a maximum power density of 400 watts per square foot is achieved at 68 percent of the open circuit voltage, or 0.325 volt. This high performance value is especially desirable when methods for raising the potential to the specified system level of 28 volts must be considered, since the higher the cell voltage, the fewer the cells required in a series connection.

6. It appears that the high initial spurious voltages observed in all previous experiments with the lithium-hydrogen fuel cell were due to impurities in the system fluids. During the recent run no such effect was observed. From initiation of the run the voltage rose smoothly to an open circuit value of approximately 0.45 volt.

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7. It is reasonable to conclude that a certain portion of the spurious voltages recorded earlier were also due to local cells created by the use of two or more materials of construction. That this effect was not alone responsible, however, was demonstrated by the fact that the spurious voltage still occurred in the all-iron cells, although much diminished from the values observed when iron or columbium diaphragms were employed in stainless steel cells. When vanadium was used as a diaphragm in an iron cell, this voltage was maintained even in the absence of both lithium and hydrogen, and continued until the diaphragm itself was consumed.

8. The electrode test apparatus is designed to measure only the performance of the electrodes, and does not reflect the cell output as affected by anode-cathode spacing, cell geometry, interval resistance, contact resistance, or the like. The values given are those which a perfectly designed cell could be expected to produce. When this system is compared to most others reported in the literature, it must be realized that the same standards are used.

The single non-IR-free value obtained toward the end of the run is a true output value, including all resistance. Unfortunately, it was obtained during the period when it was known that the anode was becoming depleted of lithium; yet a current density value of 117 amps per square foot was still recorded.

Numerous factors existed in the present cell run which must have caused high resistance in the cell. These include:

Anode-Cathode Distance

In order to assure that any droplets of lithium which might tend to protrude upward from the anode would not contact the cathode, the spacing between the two electrode was large--one half inch. Earlier work had shown that cell output could be increased markedly with a decrease in electrode spacing. It is now known that the spacing can be considerably reduced, and future work should include this design modification.

IR Drop in Cathode

The current is generated and collected over the face of the cathode and can exit to the external circuit only by passage through the foil to its edges. A mathematical study of this function shows that for a given electrode material and current density, the resistance is independent of diameter, the function for voltage drop being

$$IR = \frac{1}{4} \frac{\rho}{\pi t}$$ (3)

where rho, $\rho$, is the resistivity of the metal in ohm-centimeters, and t is the thickness in centimeters.

According to Tottle (Reference 4) the resistivity of 99.95 percent-pure columbium at 500°C (932°F) is 35.0 x $10^{-6}$ ohm centimeters, and at 600°C (1112°F) the value is 38.96 x $10^{-6}$. Assuming an average value of 37 x $10^{-6}$ at the cell temperature (550°C, or 1020°F) the IR drop in a columbium diaphragm 0.005 inch, or 0.0125 cm, thick at the optimum current of 3.34 amps is

$$ IR = \frac{I \; \rho}{4 \pi \; t} $$

or

$$ IR = \frac{3.35 \times 37 \times 10^{-6}}{4 \pi \; (0.0125)} $$

$$ = 0.0008 \text{ volt} \tag{4} $$

The loss in the diaphragm is thus seen to be quite small. A more marked drop occurs in the cathode shank, however, where the voltage drop is a function of current, resistivity, length, and area, according to the equation

$$ IR = I \; \rho \; \frac{L}{A} \tag{5} $$

For the 11-1/2-inch cathode, 3/8-inch O.D. with a 0.002-inch wall, and assuming a resistivity of 25 x $10^{-6}$ (because of the non-uniform heating of the tube), the IR drop at the same current of 3.35 amps is

$$ IR = 3.35 \times 25 \times 10^{-5} \times \frac{11.5}{0.027} $$

$$ = 0.035 \text{ volt} \tag{6} $$

The sum of these two IR drops is 0.036 volt, which is 11.2 percent of the total cell voltage at the optimum current rating. Through improved cell design this loss could be essentially eliminated, and alone would improve the non-IR-free values by more than a tenth.

## IR Drop in Anode

It may be presumed that IR loss in the porous face of the anode is essentially nil, due to its being saturated with lithium metal. Likewise the anode body, with walls 0.090-inch thick, can be ignored.

In the test cell, however, the anode body was sealed with a loose-fitting columbium plug which rested on the thermocouple well, and it was assumed before the run that contact resistance would be high. The columbium foil "star" was therefore welded to the anode, with the points bent so that the metal would be forced against the cell walls for better contact. Nevertheless,

the contact resistance must have been considerable due to the essentially point-contact nature of the connections. There is no way of determining the actual IR drop in the recent run due to this cause, but it is considered to have been high.

Careful cell design can serve to reduce internal resistance drops substantially. In earlier work with the iron electrodes it was found, for example, that reduction of the anode-cathode distance by one half nearly doubled the cell output. It is known that in addition to this aspect of design, as well as to conductivity losses in the electrode and electrode holders, a number of other variables will affect the internal resistance of the cell, and ought to be the subject of further study. These include electrolyte composition and circulation patterns, electrode shape, general cell geometry and temperature.

9.    It is reasonable that cell output in the recent run should decline with time due to the build up of lithium hydride and dissolved lithium in the electrolyte. In any attempt to study cell performance over extended periods, it will be necessary to provide means for adding lithium and fresh electrolyte and removing the by-products. This can be accomplished in the laboratory either by the use of reservoirs or a circulating regenerative system.

10.   During the early iron cell work, it was found that the variation of current density with hydrogen pressure followed the square root rule:

$$\frac{\text{current density at } P_A}{\text{current density at } P_B} = \frac{\sqrt{P_A}}{\sqrt{P_B}} \tag{7}$$

The present run was carried out at a hydrogen pressure of one atmosphere. If the square root rule can be applied, conversion of the current density obtained at optimum power level (1300 amps per square foot) to the value at a pressure of 10 millimeters, at which the regenerator is most efficient, indicates a current density of 150 amps per square foot. At 50 millimeters the calculated value is 330 amps per square foot.

It is entirely possible, however, that higher values can be realized. The permeability of columbium to hydrogen is such that at one atmosphere pressure a theoretical current density in excess of 40,000 amps per square foot is possible, so that the actual laboratory test at 3,500 amps still represents less than ten percent of the capacity of the electrode to supply hydrogen. There is no doubt that further work will uncover improved methods for achieving higher permeability, yet polarization effects, which were clearly present in the recent run after the heavy loading, are no doubt largely responsible for the relatively low output.

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But the tendency of the cell to polarize is a function of the actual current density rather than the ability of the electrode to supply fuel; that is, the phenomenon takes place in the electrolyte away from the mass of the electrode. Thus at low pressures and correspondingly lower currents, the tendency to polarize will diminish, so that it may be possible to realize a larger portion of the capacity of the electrode to supply hydrogen. Based on the permeability of the electrode alone, a theoretical current density of 4,500 amps per square foot should still be possible at a pressure of 10 millimeters.

11. There was no indication of corrosion or deterioration of any parts of the cell after the run, and no sign of any corrosion products in the salt. The embrittlement of the cathode shank and the thermocouple well were due to their having been cooled before the hydrogen absorbed during the run could be removed. There is no problem in this respect, however. In operation of a fuel cell the columbium is ductile and strong in the presence of hydrogen either at room temperature or at the temperature of operation, so that as long as hydrogen is admitted to the cell after heat up and is removed, by diffusion, evacuation, or flushing, before the cell is cooled there will be no tendency to embrittlement. Although tests of longer duration will be required before definitive specifications can be prepared, it is apparent that the purification and handling treatments described in this report are adequate for short-term runs. The concept of using columbium metal to getter any materials which will be in contact with any columbium cell parts appears to be justified, and suggests simple methods for cleaning any working system.

Other materials, such as titanium, zirconium, and yttrium, are superior getters, and are recommended for use where they will not contaminate the material which is being gettered. The use of titanium to purify lithium is satisfactory; however, these metals, as well as zirconium, are readily soluble in the eutectic salt and thus cannot be used to clean it. Of the metals which are sufficiently active as getters, only columbium is insoluble.

12. It appears that the method of cleaning process equipment by fluxing it with salt which itself is being continuously purified by exposure to a columbium getter is adequate.

The most realistic approach to cleaning a complete system would therefore probably include a columbium getter through which all system salts would be circulated. In this manner any oxygen which could be introduced from any source would be picked up by the salt, which would then give it up to the columbium. It would be relatively simple to arrange to vacuum anneal the cell and seal it prior to the final filling so that none of these contaminants could reach the cathode before the system was thoroughly purged. Since the system concept calls for introducing the salts to the cell through the anode-separator, the opening of this seal would admit salt to the cell only after it had been cleaned.

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13. The porous columbium anode, whose development was only incidental to the main objective of the work, appears to be completely satisfactory. No effort has yet been made to determine the efficiency of the anode, but it has been demonstrated to operate at a current density of 3,500 amps per square foot. Because the lithium in filling the pores presents a smooth surface, the efficiency will probably be extremely high.

Based on the recent run, there is no reason to believe that the anode as used here cannot be considered as a prototype for a final working electrode.

## 7.0 REFERENCE LIST

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